

OXALATO-AMINE-COBALT(III) COMPLEXES

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ABSTRACT. The preparation of several new octahedral oxalato-amine-cobalt(III) complexes is reported. The oxalate anion ($ox = C_2O_4^{2-}$), forms complexes of the formula $[Co(N_4)ox]Y$, where $N_4 = (NH_3)_4, (en)_2, (pn)_2, (bmen)_2, (tn)_2, (dmtn)_2, (trien), (tren)$ and $(trpn)$; $Y = Cl, ClO_4$ and PF_6 . With linear dipropylenetriamine ligand (dpt), the complexes $Co(dpt)(ox)(NO_2)$, $[Co(dpt)(ox)(H_2O)]Br \cdot 2H_2O$ and $[Co(dpt)(ox)(H_2O)]_2(ox) \cdot H_2O$ were isolated. The IR and UV-visible spectra of these complexes have been examined. Comparison of the visible spectra of the complex ions $[Co(N_4)(ox)]^+$ reveals that the relative positions of the amine ligands in the spectrochemical series follow the order: $trpn < (bmen)_2 < (tn)_2 < (NH_3)_4 < (dmtn)_2 < tren \leq (pn)_2 < (en)_2 < trien$.

INTRODUCTION

The bifunctional anions such as carbonate and oxalate are required for transferrins in order to bind metal ions; they act as "synergistic anions" [1-3]. Therefore, a number of oxalato-amine-cobalt(III) complexes have been reported [4-7]. Studying these systems may allow the opportunity to analyze the interaction of the synergistic anion with both the protein chain and the metal [8].

In this study several new oxalato-amine-cobalt(III) complexes were prepared in order to establish and check the spectrochemical order of some polydentate amine ligands. The ligands included in this study are varied from simple monodentate amine such as NH_3 , to bidentate amines such as 1,2-diaminoethane (en), 1,2-diaminopropane (pn), 1,3-diaminopropane (tn), 2,2-dimethyl-1,3-diaminopropane (dmtn) and 1,2-bis(methylamino)ethane (bmen), to linear tridentate and tetradentate amines as dipropylenetriamine (dpt) and triethylenetetraamine (trien) and to the tripodal quadridentate amines such as 2,2',2"-triaminotriethylamine (tren) and 3,3',3"-triaminotripropylamine (trpn).

EXPERIMENTAL

3,3',3"-Triaminotripropylamine tetrahydrochloride hemihydrate ($trpn \cdot 4HCl \cdot 1/2H_2O$) was prepared via $N(CH_2CH_2CN)_3$, which was catalytically hydrogenated with H_2 and Raney nickel in the presence of NaOH and acetic anhydride followed by hydrolysis with conc. HCl [9]. 1,2-Bis(methylamino)ethane (bmen) was purchased from Fluka Chemical Company. The rest of the amines were obtained from Aldrich and were used without further purification. All other chemicals were reagent grade quality.

Preparation of the complexes. Literature methods were used to synthesize the complexes $[\text{Co}(\text{pn})_2\text{CO}_3]\text{Cl}\cdot\text{H}_2\text{O}$ [10], $[\text{Co}(\text{bmen})_2\text{CO}_3]\text{ClO}_4$ [11], $[\text{Co}(\text{NH}_3)_4\text{ox}]\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$, $[\text{Co}(\text{en})_2\text{ox}]\text{Cl}\cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{tn})_2\text{ox}]\text{Cl}\cdot\text{H}_2\text{O}$, $[\text{Co}(\text{tren})\text{ox}]\text{ClO}_4$ and $[\text{Co}(\text{trpn})\text{ox}]\text{ClO}_4\cdot\text{H}_2\text{O}$ [4]. The interaction of $\text{Co}(\text{dpt})(\text{NO}_2)_3$, $\text{Co}(\text{dpt})\text{Br}_3$ and $\text{Co}(\text{dpt})\text{Cl}_3$ [12] with equimolar quantity of oxalic acid dihydrate at 70° afforded $\text{Co}(\text{dpt})(\text{ox})(\text{NO}_2)$, $[\text{Co}(\text{dpt})(\text{H}_2\text{O})\text{Br}]\cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})_2](\text{ox})\cdot\text{H}_2\text{O}$, respectively, in good yield. The complex $[\text{Co}(\text{dmtn})_2\text{CO}_3]\text{ClO}_4\cdot\frac{3}{2}\text{H}_2\text{O}$ was prepared via $\text{Na}_3[\text{Co}(\text{CO}_3)_3]\cdot 3\text{H}_2\text{O}$ as essentially described elsewhere [13]. The conversion of $[\text{Co}(\text{N}_4)\text{CO}_3]\text{Y}$ ($\text{Y} = \text{Cl}$ or ClO_4) to the corresponding oxalato species was performed by treating the aqueous carbonato complex with one equivalent of $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ at $60\text{--}70^\circ$. The counter ion in the isolated oxalato species was switched to PF_6^- by treating the aqueous solution of $[\text{Co}(\text{N}_4)(\text{ox})]\text{Y}$ with saturated solution of NH_4PF_6 . The purity of the known complexes was checked by comparing their electronic spectrum with those reported elsewhere, whereas the purity of the new isolated oxalato complexes was checked by elemental analyses.

Physical measurements. The IR spectra of the oxalato-amine-cobalt(III) complexes were recorded with a Nicolet 7199 FTIR spectrophotometer. Solid samples, between KBr plates, were examined over the range $4000\text{--}400\text{ cm}^{-1}$. UV-visible absorption spectra were obtained with a Cary 219 spectrophotometer. Elemental analyses of the complexes were performed by the microanalytical laboratory at Ciba Geigy AG., Basel, Switzerland.

RESULTS AND DISCUSSION

Syntheses. Red-orange oxalato-bis(diamine)cobalt(III) complexes have been usually prepared in good yield by heating $[\text{Co}(\text{N}_4)\text{Cl}_2]\text{Cl}$, where N_4 refers to $(\text{NH}_3)_4$ or polydentate amine(s), with sodium, potassium or ammonium oxalate and by the reaction of $[\text{Co}(\text{N}_4)\text{CO}_3]\text{Y}$ ($\text{Y} = \text{Cl}$, NO_3 , ClO_4) with oxalic acid [4-6]. In a few cases oxidation of cobalt(II) acetate was performed in the presence of oxalic acid and the diamine ligand [7].

A series of carbonatotetraamminecobalt(III) chloride or perchlorate were prepared and converted to the corresponding oxalato species by the reaction with oxalic acid. The chloride counter ion was switched to ClO_4^- or PF_6^- by treating a solution of $[\text{Co}(\text{N}_4)\text{ox}]\text{Cl}$ with a saturated solution of NaClO_4 or NH_4PF_6 , respectively. The reaction of $\text{Co}(\text{dpt})(\text{NO}_2)_3$ with equimolar quantity of $\text{H}_2\text{C}_2\text{O}_4$ afforded the pink $\text{Co}(\text{dpt})(\text{ox})(\text{NO}_2)$ complex. On the other hand, the interaction of $\text{Co}(\text{dpt})\text{Br}_3$ and $\text{Co}(\text{dpt})\text{Cl}_3$ with oxalic acid resulted in the formation of the purple crystalline complexes $[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})\text{Br}]\cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})_2](\text{ox})\cdot\text{H}_2\text{O}$, respectively. The former complex gives an immediate pale yellow precipitate with AgNO_3 solution indicating the presence of Br^- ion in the outer sphere; not coordinating to the central Co^{3+} ion. Although some of the oxalato-tetraamminecobalt(III) ions were resolved to their diastereoisomers [5,7], no attempts were made here to resolve it. Satisfactory elemental analyses were obtained for the new oxalato-amino-cobalt(III) complexes.

Infrared spectra. The infrared spectral data for the stretching frequencies of the important groups; $\nu_{\text{C=O}}$, $\nu_{\text{C-O}}$, $\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$ (lattice H_2O) of some of the synthesized oxalato series are shown in Table 1. The band assignments have been made by comparison of the spectral

data of tris(oxalato)- and hexaamine metal(III) and oxalato-tetraaminocobalt(III) complexes [14].

Table 1. The infrared spectral data^a of oxalato-amine-cobalt(III) complexes.

Complex or Complex ion	C=O str.	C-O str.	N-H str.	O-H str.
[Co(NH ₃) ₆ ox] ^b	1696, 1677	1410, 1268	-	-
[Co(NH ₃) ₄ ox]PF ₆	1707, 1670	1413, 1377, 1269	3336, 3218	-
[Co(en) ₂ ox]PF ₆	1707, 1691, 1681	1414, 1377, 1269	3312, 3228	-
[Co(bmen) ₂ ox]ClO ₄ ·H ₂ O	1724, 1661	1410, 1371, 1267	3232, 3173	3424
[Co(tn) ₂ ox]Cl·H ₂ O	1703, 1678, 1651	1414, 1389, 1241	3259, 3160, 3100	3570, 3470, 3336
[Co(dmtn) ₂ ox]ClO ₄ ·3/2H ₂ O	1703, 1685, 1646	1399, 1367, 1259	3260, 3143	3560, 3460
[Co(tren)ox]ClO ₄ ·H ₂ O	1704, 1683, 1660	1401, 1388, 1252	3286, 3249, 3166	3615, 3530
[Co(trpn)ox]PF ₆	1708, 1678	1382, 1247	3222, 3208, 3149	-
fac-[Co(dpt)(ox)(H ₂ O) ₂ ox]·H ₂ O	1695, 1677, 1635	1406, 1253	3275, 3184, 3075	3553, 3445

^aThe frequencies are reported in cm⁻¹ unit. ^bData taken from ref. [14] p. 248.

In general lattice water with hydrogen bonding absorbs at 3200-3550 cm⁻¹ due to antisymmetric and symmetric O-H stretching modes. However, the complexes, [Co(tn)₂ox]Cl·H₂O, [Co(dmtn)₂ox]ClO₄·3/2H₂O and [Co(tren)ox]ClO₄·H₂O show bands at 3570, 3560 and 3615 cm⁻¹, respectively, assigned to ν_{O-H} stretching. The absorption bands in the range 3400-3000 cm⁻¹ are attributed to the symmetric and antisymmetric N-H stretching [14]. The oxalato(tetraamine)cobalt(III) complexes under investigation display a series of bands in this region. It has been reported that the oxalato metal complexes exhibit absorption bands over the range 1630-1720 and 1240-1430 cm⁻¹ attributed to ν_{C=O} and ν_{C-O} stretching, respectively, depending on the nature and oxidation state of the metals [14]. The data collected in Table 1 are in good agreement with this expectation.

It is known that with metal ions, different coordination properties were reported for oxalate, which may act as a unidentate, a bidentate or a bridging group [15-17]. However, the bidentate chelate structure is the most common. This was confirmed for a number of the investigated complexes such as [Co(en)₂ox]Y (Y = Cl, Br, I, PF₆) and [Co(tn)₂ox]Y·H₂O (Y = Cl, Br, I) by X-ray structural determination [18]. The bidentate nature of the oxalate ion in similar complexes was also supported by ¹³C NMR study [4].

UV-visible spectra. The electronic spectra of the isolated oxalato-amine-cobalt(III) complexes, collected in Table 2 exhibit two bands in the visible region. This is consistent with octahedral geometry. The bands may be assigned to the electronic transitions ¹T_{1g} ← ¹A_{1g} and ¹T_{2g} ← ¹A_{1g} of cobalt(III) ion in the pseudo-octahedral symmetry [19]. It is evident that the amine ligands do not affect the electronic transitions drastically.

Several formulas may be assigned for each one of the complexes [Co(dpt)(ox)(H₂O)]Br·2H₂O and [Co(dpt)(ox)(H₂O)₂ox]·H₂O. The identical feature of the visible spectra for the two complexes suggests the existence of the same complex ion in the two species, which could be formulated as [Co(dpt)(H₂O)₃]³⁺ or [Co(dpt)(ox)H₂O]⁺. The

visible spectra of the complex ion, $\text{fac}[\text{Co}(\text{dpt})(\text{H}_2\text{O})_3]^{3+}$ displays two bands at 450 and 375 nm with molar absorptivities 53 and $68 \text{ cm}^{-1}\text{M}^{-1}$, respectively [20]. The two strong absorption bands detected at 532 and 380 nm for the oxalato-dipropylene-triamine complexes (Table 2) are most likely in agreement with the facile geometry [21], but rule out the formation of the triaqua species. Therefore, these results might be attributed to the existence of $\text{fac}[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})]^{+}$ ion, in which the oxalate ion is bidentate coordinating to the central Co^{3+} ion.

Table 2. Electronic spectral data of oxalato-amine-cobalt(III) complexes in water.

Complex	λ_{max} (ϵ)	
$[\text{Co}(\text{NH}_3)_4\text{ox}] \text{Cl}^{\text{a}}$	509 (80)	358 (122)
$[\text{Co}(\text{NH}_3)_4\text{ox}] \text{PF}_6$	508 (80)	356 (124)
$[\text{Co}(\text{en})_2\text{ox}] \text{PF}_6$	494 (111)	354 (153)
$[\text{Co}(\text{en})_2\text{ox}] \text{Cl}^{\text{a}}$	498 (114)	356 (142)
$[\text{Co}(\text{pn})_2\text{ox}] \text{ClO}_4$	496 (153)	354 (198)
$[\text{Co}(\text{bmen})_2\text{ox}] \text{ClO}_4 \cdot \text{H}_2\text{O}$	528 (130)	370 (110)
$[\text{Co}(\text{tn})_2\text{ox}] \text{Cl} \cdot \text{H}_2\text{O}$	510 (90)	358 (168)
$[\text{Co}(\text{tn})_2\text{ox}] \text{Cl} \cdot 1/2\text{H}_2\text{O}$	510 (79)	358 (147)
$[\text{Co}(\text{dmtn})_2\text{ox}] \text{ClO}_4 \cdot 3/2\text{H}_2\text{O}$	506 (96)	356 (175)
$[\text{Co}(\text{tren})\text{ox}] \text{ClO}_4^{\text{b}}$	497 (128)	355 (136)
$[\text{Co}(\text{trpn})\text{ox}] \text{ClO}_4 \cdot \text{H}_2\text{O}^{\text{c}}$	530 (94)	363 (199)
$[\text{Co}(\text{trpn})\text{ox}] \text{PF}_6$	532 (99)	366 (203)
<i>cis</i> - α - $[\text{Co}(\text{trien})\text{ox}] \text{Cl}^{\text{a}}$	493 (110)	357 (123)
<i>cis</i> - β - $[\text{Co}(\text{trien})\text{ox}] \text{Cl}^{\text{a}}$	497 (179)	357 (179)
$\text{Co}(\text{dpt})(\text{ox})(\text{NO}_2)^{\text{d}}$	496	
$\text{fac}[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})] \text{Br} \cdot 2\text{H}_2\text{O}$	534 (81)	379 (151)
$\text{fac}[\text{Co}(\text{dpt})(\text{ox})(\text{H}_2\text{O})_2\text{ox} \cdot \text{H}_2\text{O}^{\text{e}}$	532 (86)	380 (151)

^a Ref.5, ^bRef.6, ^cRef.4, ^dsaturated solution, ^eMolar absorptivities are estimated based on the monomeric species.

On comparing the longest wavelength absorption bands for the oxalato-tetraamine cobalt(III) complexes, $[\text{Co}(\text{N}_4)\text{ox}]^+$ (Table 2), one can conclude that the relative position of the amine ligands in the spectrochemical series increase in the order:

$\text{trpn} < (\text{bmen})_2 < (\text{tn})_2 < (\text{NH}_3)_4 < (\text{dmtn})_2 < \text{tren} \leq (\text{pn})_2 < (\text{en})_2 < \text{trien}$.

Thus among this series, trien ligand would have the strongest ligand field strength, whereas trpn has the weakest. The *N*-alkyl substituted amines (bmen) and the six-membered chelates associated with the more flexible ligands (trpn and tn) give rise to weaker fields than that exerted by five-membered chelates (trien and en). Similar order was maintained in previous studies with some of these amines [6,22,23].

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